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A NEW STUDY OF STELLAR MOLECULAR ABUNDANCES

I. The Influence of Polyatomic Molecules on Previously Determined Abundances.

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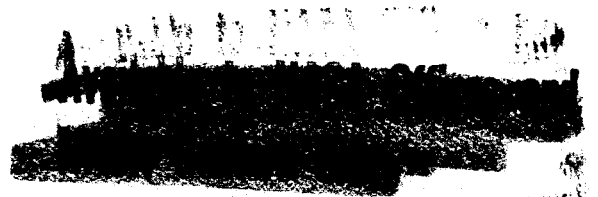
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ABSTRACT

Abundances of molecules, ions and atoms are calculated for conditions prevailing in late type dwarf, giant and supergiant atmospheres. Three different carbon to oxygen ratios are employed. Results indicate that some molecules not considered in previous investigations are of importance both in themselves and in influencing the abundance of other molecules.

The first thorough investigation of the abundances of molecules and atoms in stellar atmospheres as a function of spectral class and luminosity type was carried out by H. N. Russell (1934). Further studies of the problem have improved upon Russell primarily in their use of more accurate dissociation energies, and in the number of species they considered. With the latter point especially in view, it was considered worthwhile to carry out the solution of the relevant equations once again for a large number of molecules and ions to see how the addition of species not previously considered would alter the results based upon a fewer number of components.

For any case of species A and B in equilibrium with their compound species AB, the number densities of A, B and AB are related by

$$\frac{N_A N_B}{N_{AB}} = \frac{Z_A Z_B}{Z_{AB}}$$

where Z_A is the partition function of species A, etc. (see, for example, Fowler and Guggenheim, 1960). The partition function is related to the number of modes in which a system (here, an atom, molecule or electron) may possess

energy. Since a molecule may possess energy of translation, rotation and vibration as well as in its electronic configuration and nuclear energy state, the total partition function, which is the product of each individual partition function, assuming them to be independent, is given by

$$Z = Z_t Z_r Z_v Z_e Z_n$$

where Z_t is the translational partition function; Z_r , the rotational; Z_v , the vibrational; Z_e , the electronic; and Z_n , the nuclear. Formally, the partition function in each case is given by

$$Z_i = \sum_n \exp (-E_{in}/kT)$$

where E_{in} is the n th energy level in the i th energy mode, k is Boltzmann's constant, and T is the absolute temperature. We see that for atoms, $Z_r = Z_v = 1$, as $E_0 = 0$ in both cases, and the excited states have E_n much greater than kT .

The translational partition function is given by statistical thermodynamics as

$$Z_t = \left[\frac{2\pi M k T}{h^2} \right]^{3/2}$$

where M is the mass of the system and h is Planck's constant.

Thus,

$$\frac{N_A N_B}{N_{AB}} = \left[\frac{2\pi u k T}{h^2} \right]^{3/2} \frac{Z'_A Z'_B}{Z'_{AB}} e^{-D/k T}$$

where u is the reduced mass, given by

$$u = \frac{M_A M_B}{M_A + M_B},$$

Z'_A , Z'_B and Z'_{AB} are the internal partition functions of species A, B and AB (i.e., that part of the total partition function which does not contain the translational partition function) and D is the dissociation energy of species AB into the separate species A and B. D arises from the selection of the ground state energy of the separated species as the zero point of energy; the energies appearing in Z'_{AB} are now measured from the ground state energy of AB. This is the Saha-Boltzmann equation.

The rotational partition function for linear molecules is found to be

$$Z_r = \frac{8\pi^2 A k T}{h^2 s}$$

where A is the transverse moment of inertia of the molecule. s, the symmetry number, is the number of indistinguishable orientations of the molecule (e.g., 2 for C₂, 12 for CH₄). Rotation about the axis joining the nuclei has such a large separation of the energy eigenvalues that its partition function equals one for our purposes. For non-linear polyatomic molecules,

$$Z_r = \frac{8\pi^2}{s} \left[\frac{2\pi k T}{h^2} \right]^{3/2} (A B C)^{1/2}$$

where A, B and C are the molecule's three principal moments of inertia.

The vibrational partition function is

$$Z_v = \prod_i (1 - \exp \left[-h \nu_i / k T \right])^{-1}$$

where ν_i is the characteristic frequency of the *i*th mode of vibration. For example, a diatomic molecule has only one mode of vibration; thus, only one term would appear in its vibrational partition function.

The electronic partition function is

$$Z_e = \sum_i w_i \exp (-E_i / k T)$$

where E_i is the energy of the i th electron level above the ground level, and w_i is the statistical weight (degeneracy) of that level. In this paper, only terms in the sum where E_i was less than 2.35 ev were included, as higher terms than these were negligible in comparison with the ground level term. The infinite sum leads to no difficulty, as in reality an infinite number of electronic levels does not exist. This results from the existence of the potential fields of other particles, a phenomenon which appears as the lowering of the apparent ionization potential (or "pressure ionization") of atoms under high pressure. For atoms,

$$w_i = (2 L_i + 1) (2 S_i + 1)$$

where L_i is the orbital angular momentum quantum number of the i th level, and S_i is its spin quantum number. For molecules,

$$w_i = D_i (2 S_i + 1)$$

where S_i is once again the electronic spin quantum number, and D_i equals one if $\Lambda_i = 0$ (a Σ state) and two otherwise. Λ_i is the quantum number of the electronic angular momentum

about the internuclear axis. The behavior of D_J results from the treatment of the molecule as a rigid rotator for $\Lambda = 0$ and a symmetric top for $\Lambda \neq 0$: the symmetric top has a positive and negative rotational level for each value of J , the total angular momentum of the molecule, while the rigid rotator's rotational levels are positive or negative according to whether J is even or odd.

Since nuclear partition functions will clearly cancel in the Saha-Boltzmann equation, they need concern us no further. The only exception occurs in the case of ionization, where the electron's internal partition function has a value of 2 (the statistical weight of its free state, caused by the two possible orientations of its spin).

Together with the constraining equations on the total number of nuclei and electrons, the set of Saha-Boltzmann equations so obtained for a given number of species represents a determinate system for any given temperature and pressure. Note particularly that the electron pressure need not be assumed, but can be found simultaneously with the number densities of all other species. The number of variables is usually reduced by means of the constraining equations on the number of nuclei present. For titanium,

for example, the total nuclear number density, N'_{Ti} , is

$$\begin{aligned}
 N'_{Ti} &= N_{Ti} + N_{TiO} + N_{Ti^+} \\
 &= N_{Ti} + \frac{N_{Ti} N_O}{Q_{TiO}} + \frac{N_{Ti} Q_{Ti^+}}{N_e} \\
 &= N_{Ti} \left[1 + \frac{N_O}{Q_{TiO}} + \frac{Q_{Ti^+}}{N_e} \right]
 \end{aligned}$$

where N_{Ti} is the number density of atomic titanium present, N_O , of atomic oxygen, N_e , the free electron number density, and Q_{TiO} and Q_{Ti^+} are the ratios of partition functions found in the appropriate Saha-Boltzmann equations for N_{Ti^+} and N_{TiO} , the number densities of once ionized titanium and titanium oxide, respectively. Since N'_{Ti} is given by the relative nuclear abundances assumed, N_{Ti} may be replaced in all other constraining equations by the expression

$$N_{Ti} = N'_{Ti} / \left[1 + \frac{N_O}{Q_{TiO}} + \frac{Q_{Ti^+}}{N_e} \right]$$

When the problem has thus been reduced to seven or eight variables, a Newton-Raphson iteration brings rapid convergence from suitable initial guesses to the final solution.

To apply the investigation with rigor to a specific star, a model atmosphere would be required. Values of temperature

and pressure at every point would then lead to the various abundances at every optical depth. The results could then be compared with those derived from absorption bands in the stellar spectrum, which are themselves formed over a range of temperatures and pressures, usually different for different molecules. Needless to say, such a procedure can not at present be followed, as the atmospheres of such stars are not sufficiently well known. Thus, we adopt Aller's (1960) values of temperature and pressure for dwarfs (luminosity type V), giants (III) and supergiants (I) at optical depth $\tau_{5000} = 0.4$ and calculate the abundances there. The results can thus be regarded as a semi-quantitative guide to the effects of spectral class (or temperature), luminosity type (or pressure) and composition differences upon the abundances in stellar atmospheres.

The molecular and atomic constants employed in calculating the partition functions are listed in Table I. It was decided to adopt Aller's method of varying the carbon content so that the results could be compared directly to his (Aller, 1960, 1963, 1961). The nuclear abundances adopted are listed in Table II. The oxygen rich mixture corresponds to normal (G, K and M) stars, while the other two mixtures refer to carbon (C or R and N) stars. The effects of altering the zirconium nuclear abundance upon

the relative abundances of the oxides of titanium and zirconium have been well documented elsewhere, and thus only one zirconium nuclear abundance was employed. The characteristic parameters of ZrO_2 and TiO_2 were not considered sufficiently well known to warrant the inclusion of these molecules. Stanger (1963) has shown, however, that the TiO and ZrO abundances are depressed at lower temperatures by the formation of the dioxides. Table III gives the empirical temperature - spectral class relationship for the three luminosity types considered for $t_{5000} = 0.4$. Since molecular absorption is most important in the infrared, the temperature of the region in which some absorption lines are formed in a star of given spectral class may be lower than that given in Table III.

Iben (1964) has proposed that during its helium burning phase the nitrogen to carbon nuclear abundance ratio at the surface of a red giant may rise to values greater than 1. A series of solutions for equal nitrogen and carbon nuclear abundances was therefore carried out to provide a basis for the observational check of Iben's theory.

NORMAL COMPOSITION STARS

Figures 1, 2 and 3 show the results of our calculations for dwarfs, giants and supergiants of normal (oxygen rich) composition. As in Aller, molecular hydrogen becomes the most important component in dwarfs for temperatures below 3100° K. Water is more abundant than OH for temperatures below 3100° K, and, below 4200° K, more abundant than CH, which reaches a maximum at 4600° K and becomes much less abundant at low temperatures. N_2 is the most abundant nitrogen compound, being more abundant than atomic nitrogen below 3800° K. Cyanogen (CN) reaches a maximum at 4200° K. The TiO and ZrO abundances and behavior agree with Aller's calculations. It is seen that CO_2 , CH_2 , CH_3 , CH_4 , CS and HCN are the molecules which absorb most of the carbon left over from CO at low temperatures, thus depressing the abundances of C_2 , CH and CN. Methane is more abundant than cyanogen for temperatures below 2600° K. Among other prominent compounds not considered by Aller are NH_3 , SH, H_2S , SiO, MgH, MgO and S^- . Ammonia rises to one-fiftieth the NH abundance at 2500° K. Silicon monoxide is more abundant than OH at 2500° K, being about one-tenth the carbon monoxide abundance there. The negative sulfur ion abundance becomes one-quarter that of H^- at 2500° K.

For giants of the same composition, our calculations agree with Aller as to oxygen being more abundant than carbon monoxide to the lowest temperatures considered. Likewise, molecular hydrogen (H_2) never becomes as abundant as atomic hydrogen. Water is down by a factor of 10 in concentration relative to the dwarf, or by a factor of 200 relative to the atomic hydrogen abundance. Titanium, zirconium and their oxides also exhibit the behavior found by Aller. Silicon monoxide, which he did not consider, is the sixth most abundant molecule at low temperatures, after H_2 , CO, OH, H_2O and N_2 . CN and C_2 reach maxima around 4500° K, but are severely depleted at lower temperatures by the formation of CO_2 . CH_2 is more abundant than CH below 2900° K but its concentration at low temperatures is down by three orders of magnitude from the dwarf. CH_2 and HCN both exhibit maxima around 3900° K. Ammonia abundances for the giant are always 10^5 less than NH abundances.

In supergiants, the behavior of carbon monoxide, molecular and atomic hydrogen, titanium, zirconium, and their oxides, and N_2 agrees with Aller's calculations. C_2 , however, as well as CN and CH, ^{is} ~~are~~ depleted at low temperatures by the formation of carbon dioxide. C_2 and CH attain maxima at 4200° K, and CN at 3900° K. CO itself

has a flat maximum at 3600° K. Water is down from its concentration in giants by another order of magnitude. CH_3 and CH_4 are much less abundant than CH or CH_2 . Silicon monoxide, however, is more abundant than OH between 2500° K and 2800° K. Ammonia is down by a factor of 10 from its concentration in giants.

CARBON STARS

Stars containing anomalously large abundances of carbon relative to oxygen are observed only as giants or supergiants. Figures 4 and 5 show the results of the calculations for these two types when the carbon and oxygen abundances are equal. As with Aller's results, CN is much more abundant than in a star of normal composition, reaching a maximum at 3900° K in the giant and 3600° K in the supergiant. In both types it continues to be abundant down to low temperatures. The oxides of titanium and zirconium are down by 10^4 and 10^3 from their normal abundances, solely due to the increased absorption of oxygen in carbon monoxide. All other carbon compounds, with the exception of CO_2 , are up by a factor of 10^4 at temperatures below 4000° K from their concentration in stars of normal composition, and

oxygen compounds are down by a factor of 10^4 . Oxygen is now tied up in carbon monoxide, and is thus unable to form more of the dioxide. CS is found to be the next most abundant carbon compound after CO, being more abundant than cyanogen below 3300° K in the giant and 3100° K in the supergiant. CH_2 becomes the most abundant hydrocarbon at lower temperatures. SiO is the most abundant oxygen compound after carbon monoxide, exhibiting a flat maximum around 2500° K. SiH and SH are also abundant. Molecular hydrogen remains below atomic hydrogen in giants by a factor of 4 even for temperatures around 2500° K.

Figures 6 and 7 show the abundances found in the extreme case of carbon rich giants and supergiants. As in previous studies, H_2 and CO are the most abundant molecules. The oxides of titanium and zirconium are depressed still further, with a flat TiO maximum at 3100° K in the supergiant and 3600° K in the giant. C_2 is more abundant than CN below 2800° K, but is always less abundant than atomic carbon. CH_2 is more abundant than CH for temperatures below 2900° K in both the giant and supergiant, where its concentration at lower temperatures is much enhanced compared to its concentration in stars of normal composition. HCN and CS are likewise abundant in carbon rich stars.

Silicon monoxide, with a maximum at 4000° K, is down by a factor of 10^3 at low temperatures from its concentration in stars of equal carbon and oxygen abundance.

Even for these carbon rich atmospheres, the negative hydrogen ion is 300 times more abundant than the negative carbon or oxygen ions. This compares with an H^- to C^- ratio above 4500° K of 600 for equal carbon and oxygen nuclear abundances and of 2000 for normal abundance stars, a result in agreement with previous work (Branscomb and Pagel, 1958). O^- is more abundant than C^- by a factor of 10 for normal stars, and C^- becomes even less abundant below 4500° K. Thus, C^- and O^- do not seem important as sources of continuous opacity in stellar atmospheres, especially in cooler stars (Myerscough and McDowell, 1964). S^- , however, appears to be the most abundant negative ion besides H^- at low temperatures, and may be important as a source of continuous opacity in cooler giants and supergiants, where it reaches one-fiftieth the H^- abundance, or in cool dwarfs, where it attains one-fourth the H^- abundance.

STARS WITH ANOMALOUS NITROGEN ABUNDANCES

One final calculation was made for the case of giants (luminosity class III) containing a nuclear abundance of

nitrogen equal to their carbon nuclear abundance. The nuclear abundances of carbon, oxygen and all other elements except nitrogen remained the same as for the normal (oxygen-rich) star. The only differences in composition from a star of normal nuclear abundances occur, as might be expected, in molecules containing nitrogen. Such molecules as NH , NO , N_2 and CN are more abundant by factors running from 1.5 (at 2500°K) to 3 (at 4600°K) in the high abundance nitrogen star than in the normal giant. Atomic nitrogen and such less abundant molecules as HCN , NS , SiN and NH_3 exhibit the same behavior. Since nitrogen compounds containing other atoms (such as CN or NO) are much lower in abundance than the most abundant compounds containing these other atoms, increases by factors of 3 in the nitrogen compound abundances have no effect upon the abundances of molecules containing no nitrogen. Thus, any observational check of Iben's (1964) hypothesis concerning the ratio of nitrogen to carbon on the surface of red giants during helium burning must rest upon a spectroscopic investigation of the abundances of the nitrogen compounds alone.

Quantitative as well as qualitative agreement was noted between our results and those of Aller (1960) for giants of equal carbon and oxygen nuclear abundance.

Adjusting our atomic hydrogen abundance to his gives identical results for many of the compounds he lists in his Table 14. The exceptions are carbon and oxygen compounds, which are depressed in our results due to the inclusion of CS, HCN, CH₂ and SiO. Zirconium differences are due to a different composition which Aller uses to explain the S class spectrum. We also note that the electron pressures computed by us as part of the solution agree with those values he gives in his Table 7.

The greatest errors in the present calculations arise from the experimental uncertainties in the dissociation energies, which enter the equations exponentially. Fortunately, these values are known with fair accuracy for the more important molecules. It was found that the separate species are only weakly interdependent, so that errors in the dissociation energy of any one molecule will affect the abundance of that molecule alone. Further errors may be due to the exclusion of other species whose characteristic parameters are poorly known, but whose inclusion might depress the concentration of the less abundant molecules in our solutions. Further, the equations pre-suppose thermodynamic equilibrium, which is only a first approximation to conditions in the outer atmospheres of late type stars. With

these points in mind, we believe that the solutions given in this paper represent a closer approximation to the real relative abundances than previous results.

It is a pleasure to acknowledge many helpful discussions with Dr. A. G. W. Cameron, who initially suggested the problem discussed in this paper.

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TABLE I

Adopted Molecular and Atomic Constants

Species	I. P. (ev.)	Vibrational Constant $\theta_v = hv/k$	Rotational Constant $Q(\text{c.g.s.})$
Al	5.95		
H	13.5		
K	4.31		
Na	5.11		
Tl	6.82		
Zr	6.94		
C ⁻	1.13		
H ⁻	0.754		
O ⁻	1.46		
S ⁻	2.07		
Si ⁻	1.80		
H ₂	15.6	3.21 (H ₂ ⁺) x 10 ³ °K	0.611 x 10 ⁻² (H ₂ ⁺)
O ₂	12.5	2.70 (O ₂ ⁺)	10.9 (O ₂ ⁺)
OH ⁻	1.8	5.25	1.93
Molecule	ΔD (ev.)	Vibrational Constant $\theta_v = hv/k$	Rotational Constant $Q(\text{c.g.s.})$
*C ₂	6.25	2.34 x 10 ³ °K	11.2 x 10 ⁻²
*CH	3.47	3.99	2.52
CH ⁺ → C + H ⁺	3.60	3.99	2.57
CH ₂ → CH + H	5.92	2.08, 4.27, 4.32	4.48
CH ₃ → CH ₂ + H	3.40	1.95, 2.09(2), 4.27, 4.38(2)	1.50(N)
CH ₄ → CH ₃ + H	4.21	1.88(3), 2.20(2), 4.20, 4.35(3)	0.710(N)
*CN	7.5	2.95	19.2
*CO	11.1	3.10	18.9
CO ₂ → CO + O	5.40	0.960, 2.00, 3.36	89.2
CS ₂	7.9	1.84	44.4
*H ₂	4.47	6.10	0.300
H ₂ → H + H	4.91	1.02, 3.00, 4.77	47.0
HeH ⁺ → He + H ⁺	1.90	4.86	1.89
*H ₂ O → H + OH	5.11	2.29, 5.27, 5.44	0.838(N)
H ₂ S → H + SH	3.93	1.71, 3.76, 3.78	2.44(N)
K ₂	0.513	0.133	325
KH	1.89	1.39	10.7
MgH	2.0	2.10	6.29
MgO	4.5	1.13	63.7
*N ₂	9.76	3.34	9.07

TABLE I, cont.

Adopted Molecular and Atomic Constants

Molecule	D (ev.)	Vibrational Constant $\theta_v = hv/k$	Rotational Constant $Q(\text{c.g.s.})$
*NH	3.76	$4.75 \times 10^3 \text{ }^\circ\text{K}$	4.13×10^{-2}
NH ₂ → H + NH	0.44	0.917, 1.41, 2.21	4.35
NH ₃ → H + NH ₂	7.81	1.34, 2.34(2), 4.80, 4.92(2)	1.72(N)
*NO	6.59	2.69	21.4
NO ₂	3.12	1.09, 1.89, 2.33	86.3(N)
N ₂ O → O + N ₂	1.71	0.848, 1.84, 3.20	166
NS	5.0	1.74	39.1
*O ₂	5.11	2.23	12.6
O ₃ → O ₂ + O	1.02	1.01, 1.49, 1.60	65.1(N)
*OH	4.39	5.25	1.93
S ₂	4.4	1.04	61.7
SH	3.59	3.42	3.85
SO	5.35	1.61	51.5
SiH	3.19	2.99	4.85
SiN	4.5	1.66	49.7
SiO	8.09	1.78	50.3
SiS	6.38	1.07	120
*TiO	6.89	1.44	68.0
*ZrO	7.79	1.34	58.8

Molecules marked by an asterisk are those considered by Aller (1960, 1961, 1963).

In the vibrational constant θ_v , e.g., in CH₃, 2.09(2) means that the mode whose characteristic temperature is $2.09 \times 10^3 \text{ }^\circ\text{K}$ is doubly degenerate, etc.

The rotational constant, Q , $= 8\pi^2 A k/h^2 s$, where A is the transverse moment of inertia and s , the symmetry number, except for non-linear molecules, denoted by (N), where $A = (8\pi^2/s) (2\pi k/h^2)^{3/2} (ABC)^{1/2}$, A , B and C being the principal moments of inertia.

TABLE II

Adopted Nuclear Abundances

Nucleus	Relative Abundance
H	1.0×10^6
He	1.55×10^5
O	8.00×10^2
Ne	5.28×10^2
N	9.52×10^1
Si	3.15×10^1
Mg	2.51×10^1
S	2.00×10^1
Na	2.00
Al	1.60
K	5.00×10^{-2}
Ti	4.79×10^{-2}
Zr	1.70×10^{-4}
C (C rich)	1.60×10^3
C (C = O)	8.00×10^2
C (O rich)	2.50×10^2
N (C = N)	2.50×10^2
$\log A = \log (H/\text{metals}) = 4.23$	

All abundances, except those of carbon and oxygen, are solar abundances taken from L. Goldberg, E. Muller and L. Aller, Ap. J. Suppl., 5, 1, 1960.

TABLE III

Spectral Class - Temperature for Normal Stars

$$\theta = 5040/T$$

	G0	G2	G5	G8	K0	K1	K2
V	-	-	-	-	-	-	-
III	-	-	-	1.12	1.14	-	1.18
I	1.0	1.15	1.19	1.26	1.31	1.36	1.41
	K3	K5	K6	K8	M0	M1	M2
V	-	-	1.22	1.31	1.40	-	1.51
III	1.23	1.39	-	-	1.50	1.58	1.63
I	1.46	1.51	-	-	1.57	1.63	-
	M3	M4	M5	M6	M8		
V	-	1.59	-	1.70	1.84		
III	1.69	1.77	1.84	1.98	-		
I	-	-	-	-	-		

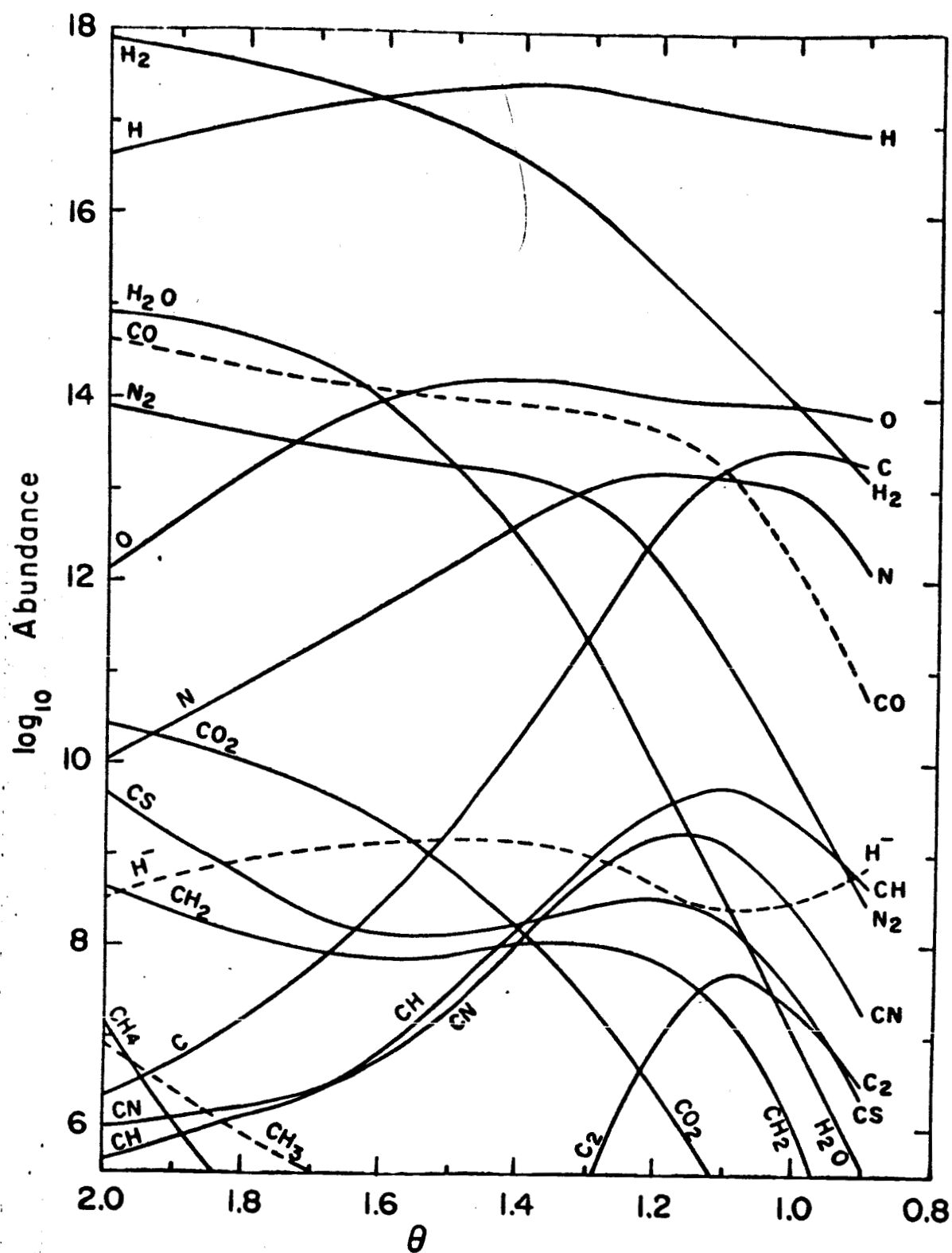


Figure 1a.
Oxygen rich dwarfs (V)

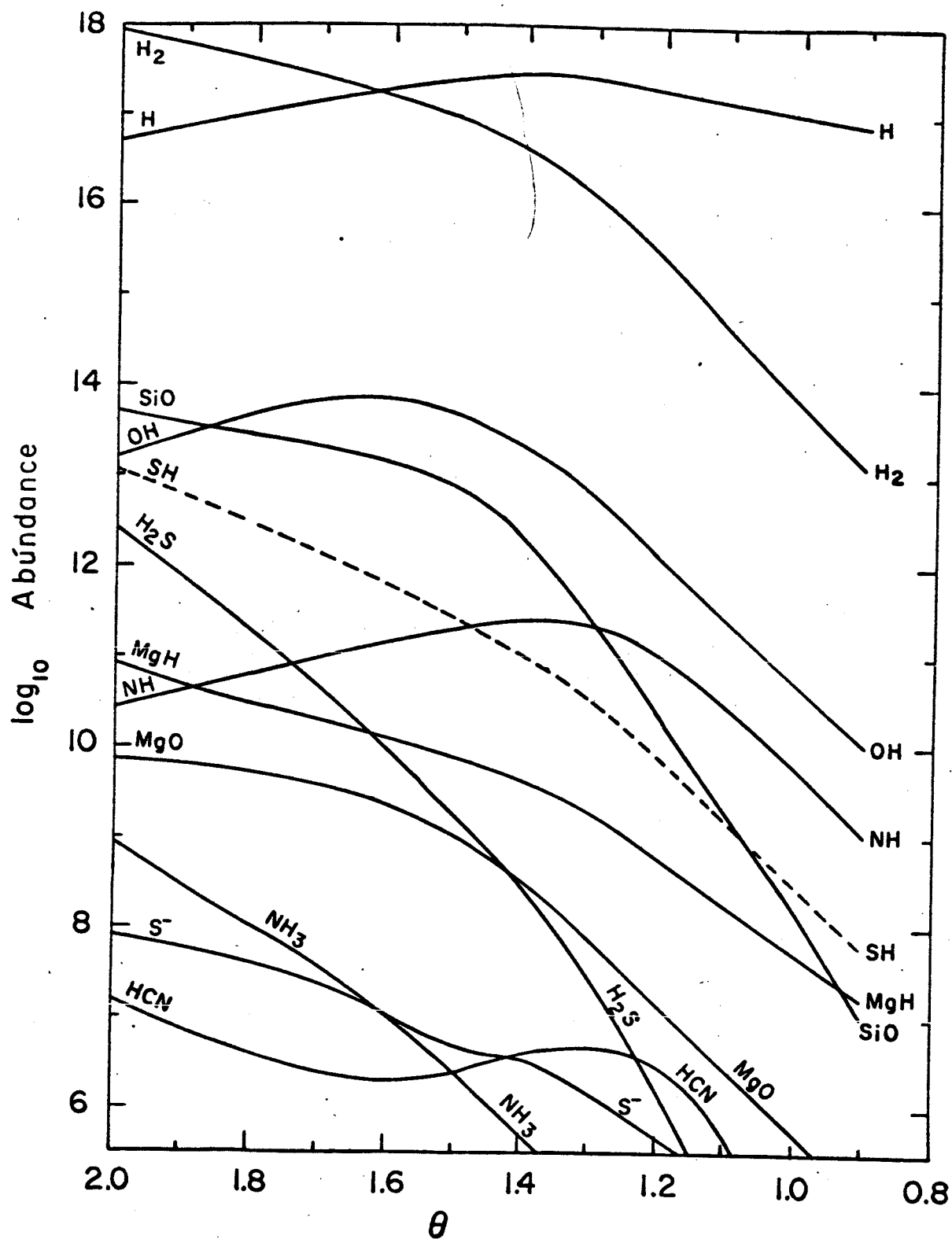


Fig. 1b.
Oxygen rich dwarfs (V)

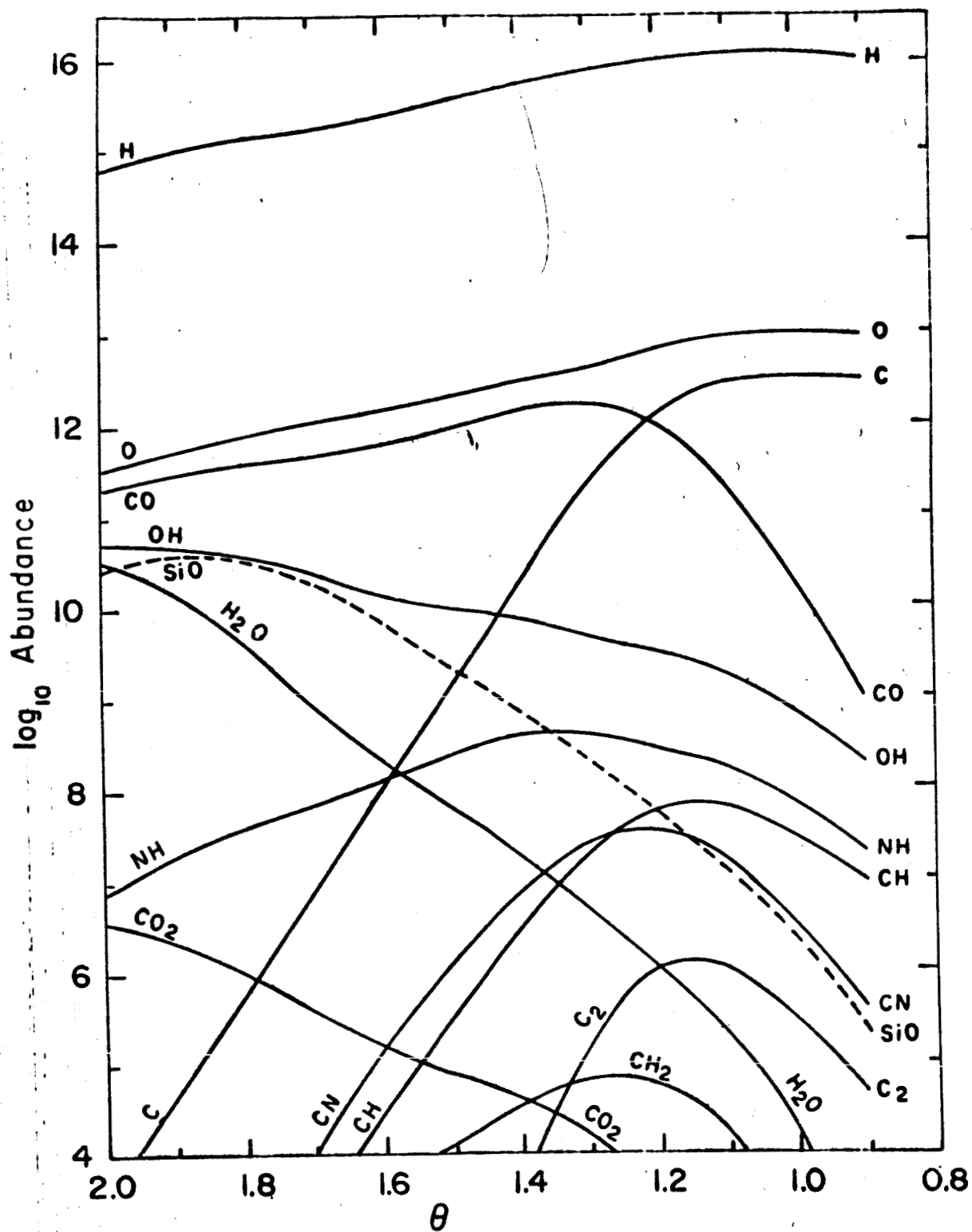


Figure 2.
Oxygen rich giants (III)

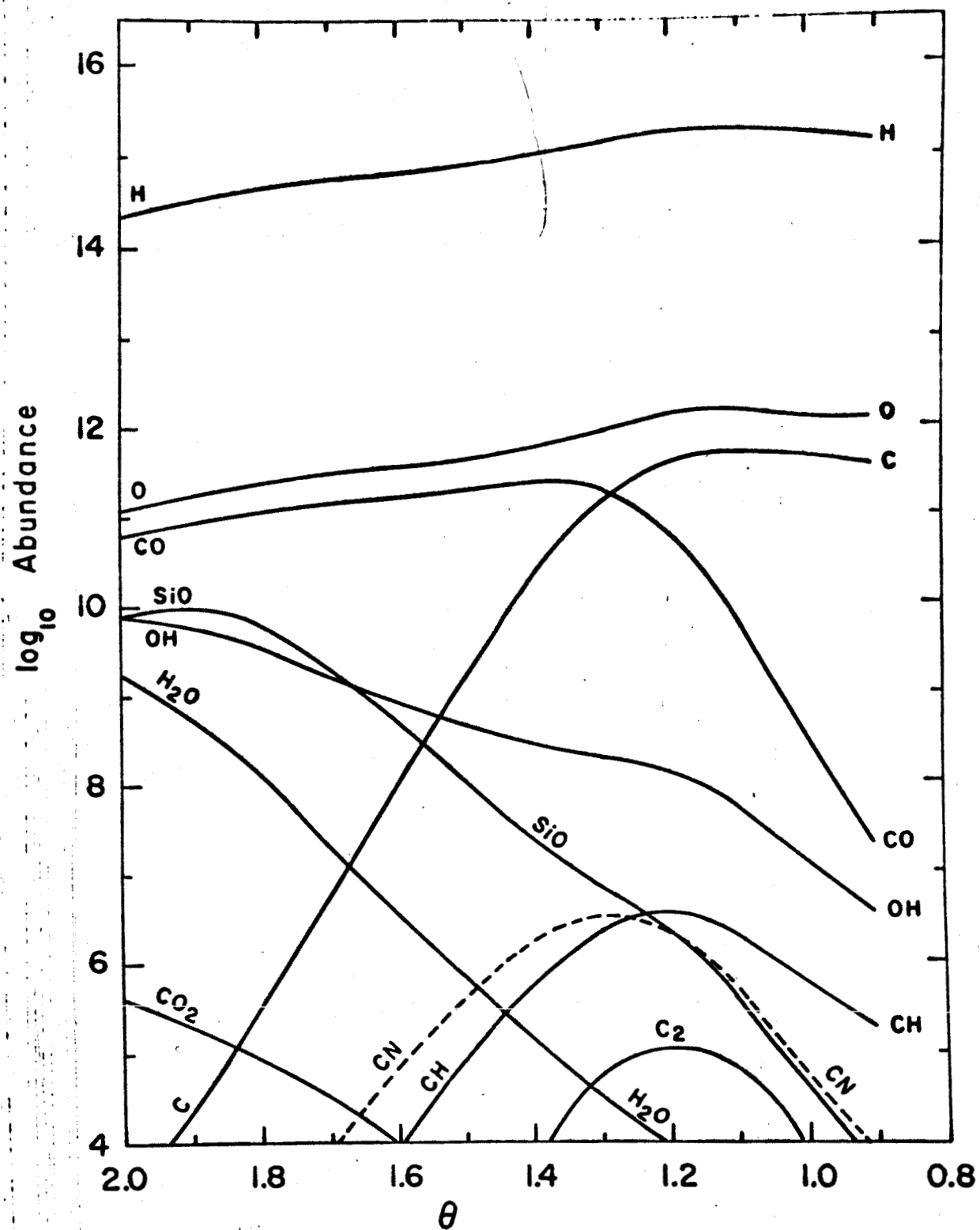


Figure 3.
Oxygen rich supergiants (I)

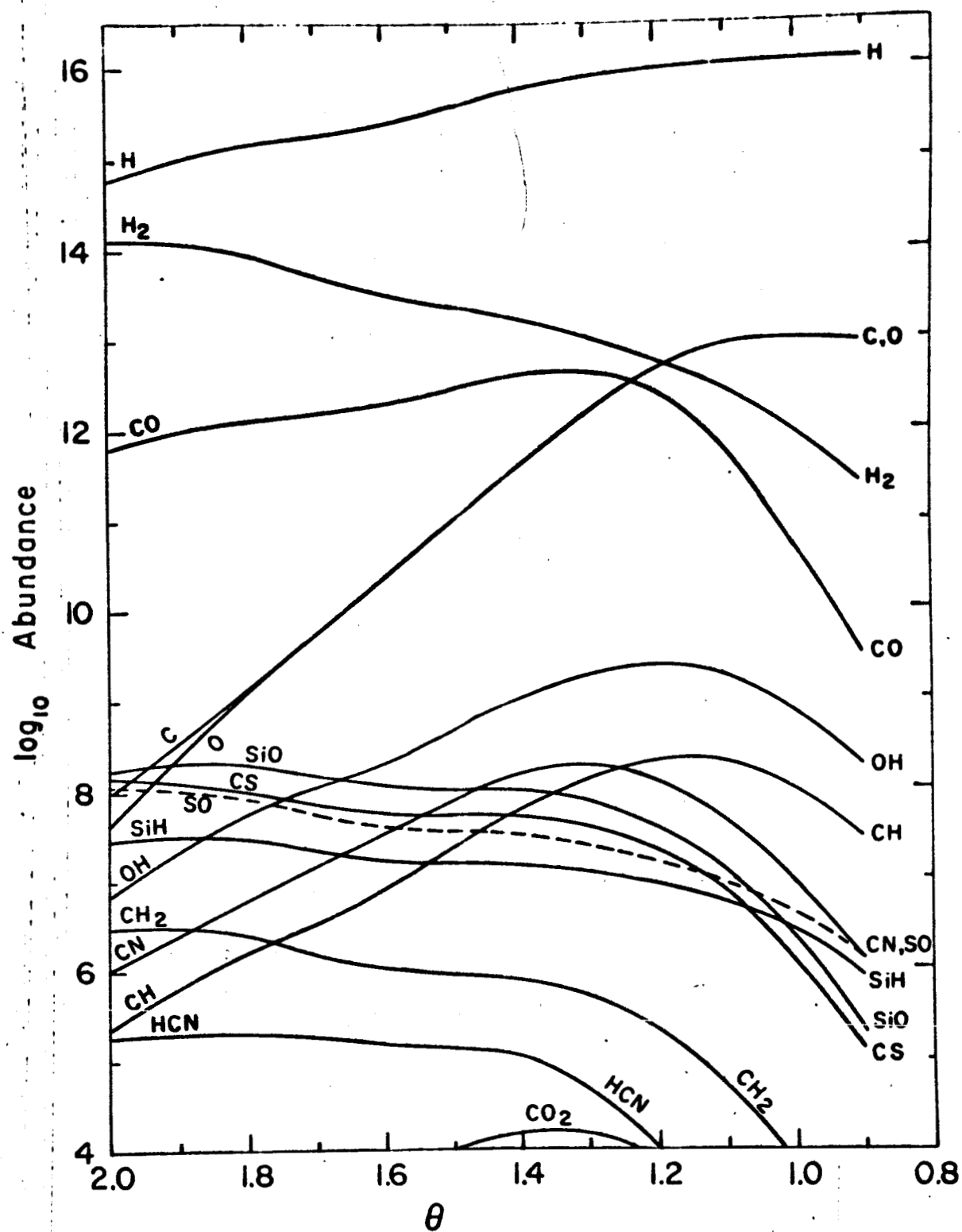


Figure 4.
Carbon-Oxygen equal giants (III)

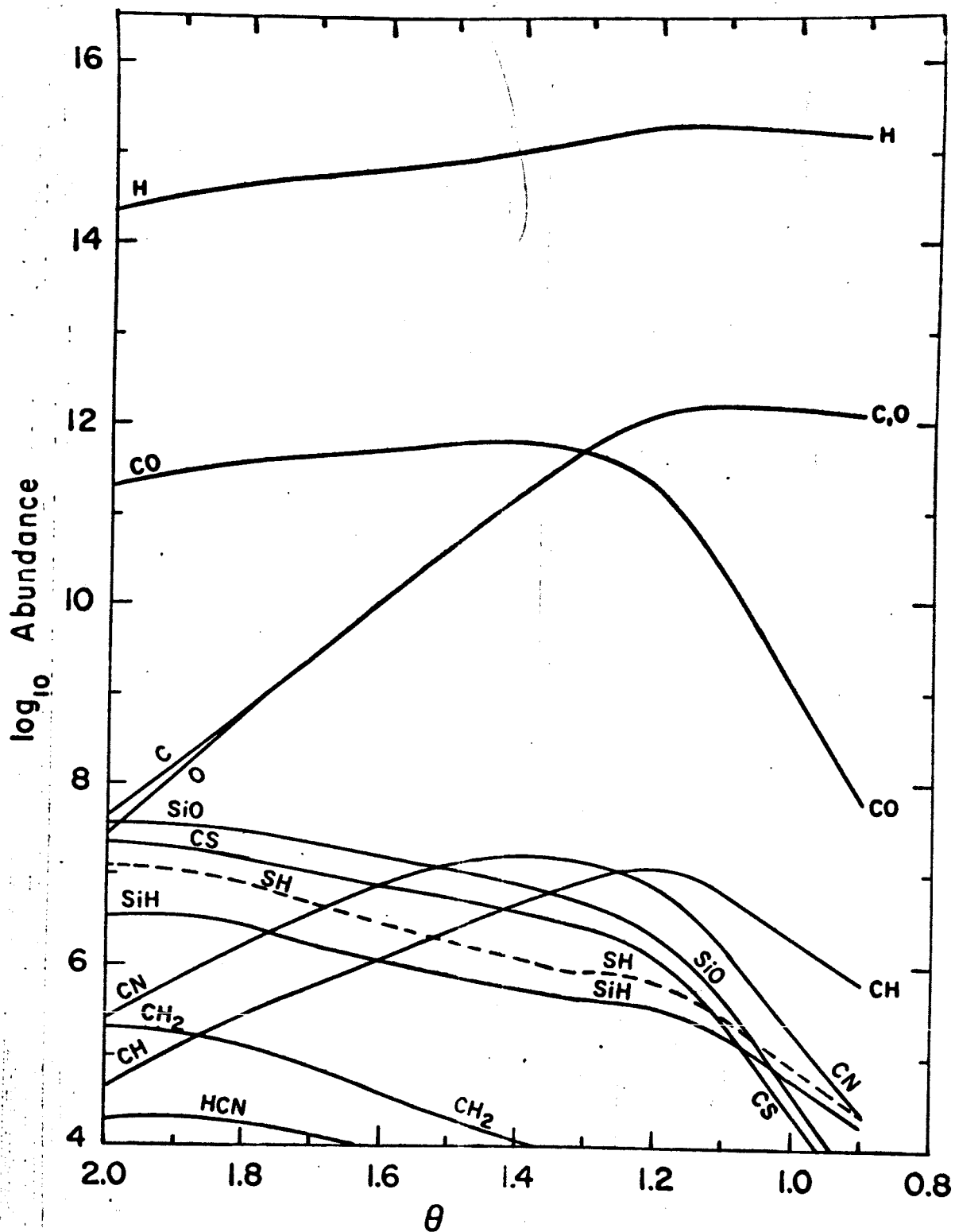


Figure 5.
Carbon-Oxygen equal supergiants (I)

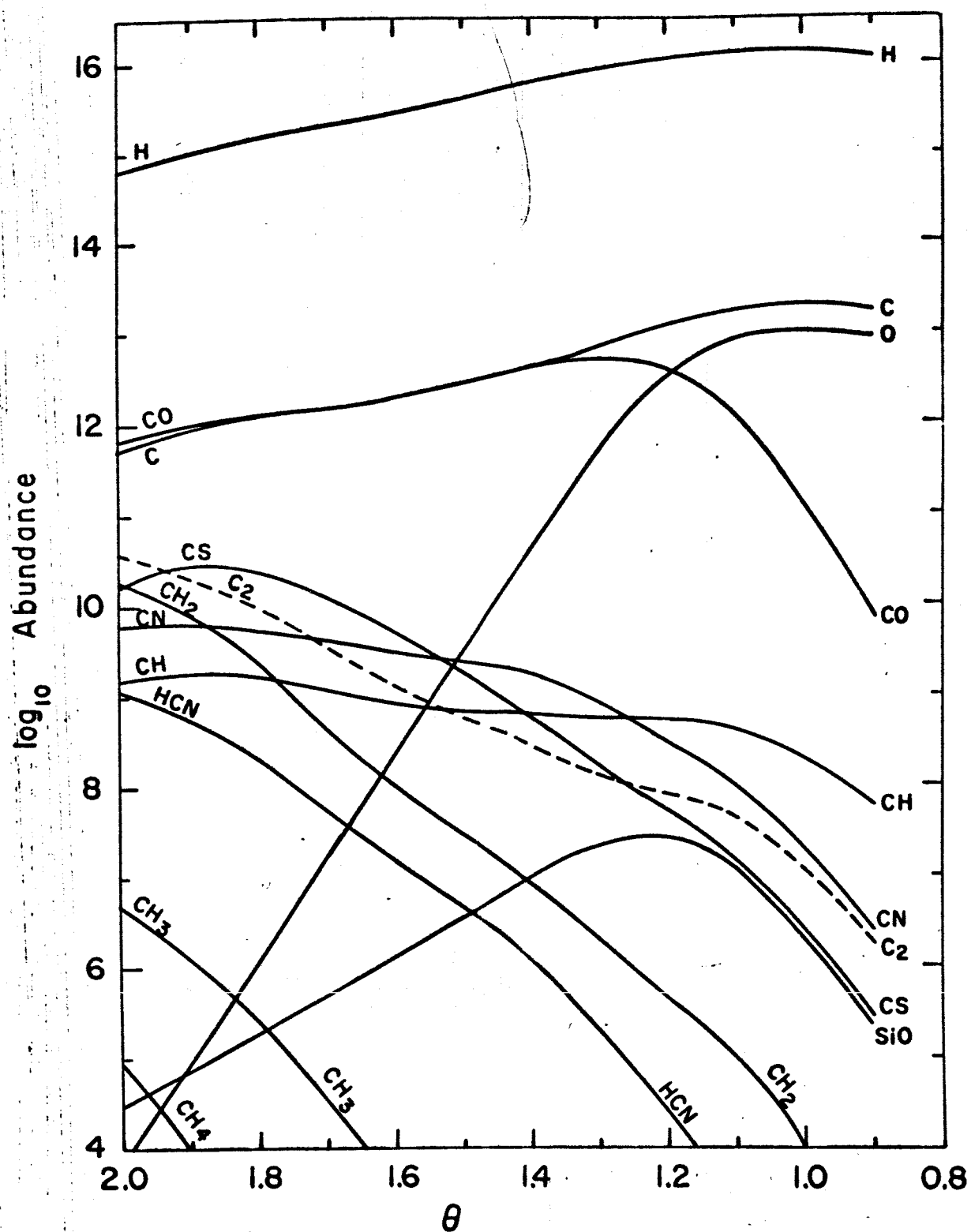


Figure 6.
Carbon rich giants (III)

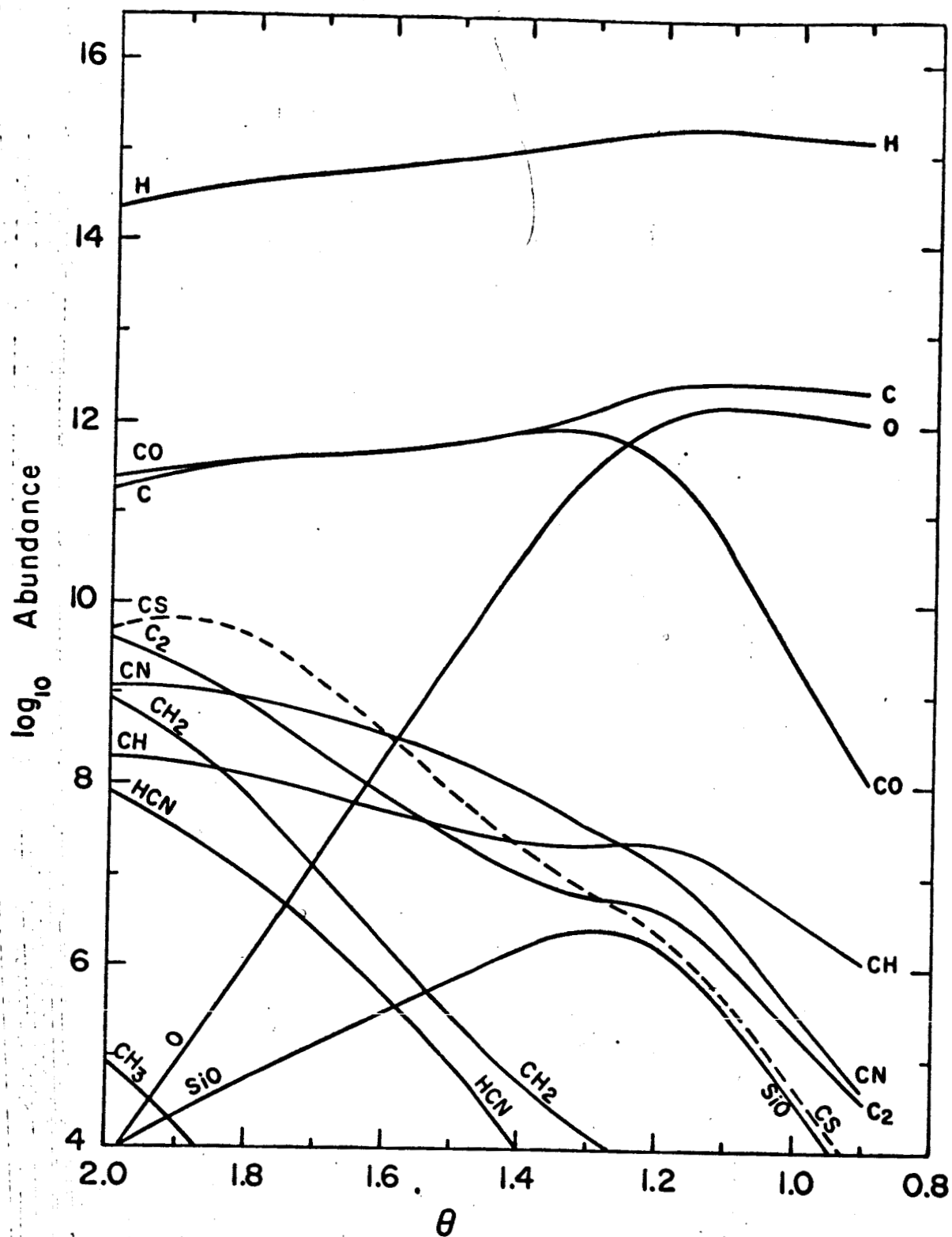


Figure 7.
Carbon rich supergiants (I)